



# Gibbs Free Energy and Relationships

- 1) Exams will most likely be graded by Wednesday
- 2) Regrade requests must be made by section Friday.
- 3) Free Energy, the puzzle and Temperature, Pressure, Volume and Phase

Reading: Last half of Chapter 3, pp. 84-114, and Chapter 4, pp.123-134



# Gibbs Free Energy

The Gibbs Free Energy is a direct measure of spontaneity:

$$G = H - TS$$

It sums up, in a way, the competition between energy considerations and “configurational” barriers.

We have also learned that a process is spontaneous if

$$\Delta G < 0$$

Thus, if

$\Delta H < 0$  the process is exothermic (downhill)

$\Delta S > 0$  the process increases disorder

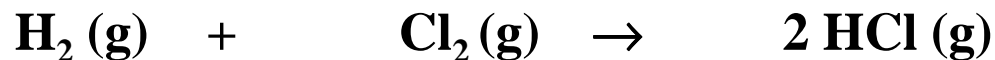
So

H dominates spontaneity at low temperatures

S dominates spontaneity at high temperatures

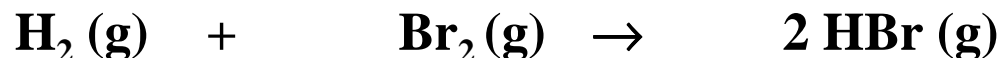


## Some instructive examples



Is  $\Delta S^\circ_{298}$  greater than, less than, or equal to zero?

$$\begin{aligned}\Delta S^\circ_{298} &= -(130.684 + 223.066) + 2 (186.68) \text{ J/(K mol)} \\ &= \mathbf{19.61 \text{ J / (K mol)}}$$



Is  $\Delta S^\circ_{298}$  greater than, less than, or equal to zero?

$$\begin{aligned}\Delta S^\circ_{298} &= -(130.684 + 245.34) + 2 (198.48) \text{ J/(K mol)} \\ &= \mathbf{20.94 \text{ J / (K mol)}}$$

*Why are these the same? How come they're not zero?*



## Some instructive examples

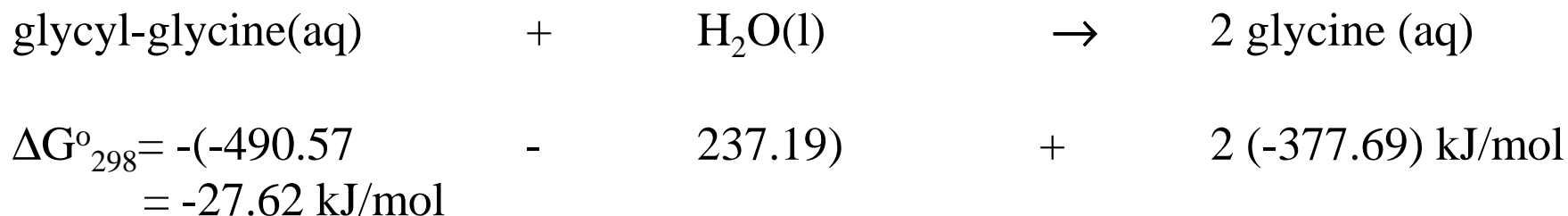


Is  $\Delta S^\circ_{298}$  greater than, less than, or equal to zero?

$$\begin{aligned}\Delta S^\circ_{298} &= -(5.69 + 205.03) + 213.64 \text{ J/(K mol)} \\ &= \mathbf{2.92 \text{ J / (K mol)}}$$



## Some instructive examples



The process is *spontaneous*!

Many proteins have this dipeptide.

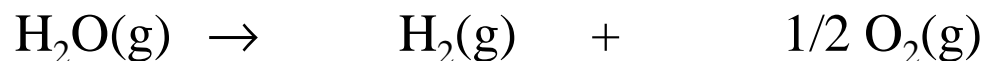
How come we don't spontaneously fall apart?

- 1) Replenishment
- 2) Kinetics

But we also have catalysts for this process!



## Some instructive examples



Is  $\Delta S^\circ_{298}$  greater than, less than, or equal to zero?

$$\begin{aligned}\Delta S^\circ_{298} &= -(188.82) + 130.684 + \frac{1}{2} (205.14) \text{ J/(K mol)} \\ &= 44.4 \text{ J / (K mol)}\end{aligned}$$

Spontaneous?

$$\Delta H^\circ_{298} = -(-241.82) + 0 + \frac{1}{2} (0) \text{ kJ/mol} = 241.82$$

$$\begin{aligned}\Delta G^\circ_{298} &= \Delta H^\circ_{298} - T \Delta S^\circ_{298} = 241.82 \text{ kJ/mol} - (298 \text{ K}) * 0.0444 \text{ kJ/(K mol)} \\ &= 228.56 \text{ kJ/mol}\end{aligned}$$

The process is *non-spontaneous*!



# Gibbs Free Energy: Basic Dependencies

So we have defined  $\Delta G$  as:

$$\Delta G = \Delta H - \Delta(TS)$$

We can substitute for  $\Delta H$  :

$$\Delta G = \Delta E + \Delta pV - \Delta TS$$

$$dG = dE + pdV + Vdp - TdS - SdT$$



Then for systems doing PV work *only*

$$\begin{aligned}dG &= dq - pdV + pdV - VdP - TdS - SdT \\ &= dq + VdP - TdS - SdT\end{aligned}$$

Remembering that  $TdS \geq dq$

$$\begin{aligned}dG &\leq TdS + VdP - TdS - SdT \\ dG &\leq +VdP - SdT\end{aligned}$$

So for an open system at constant T and P, the criterion for spontaneity is:

$$dG \leq 0 \left\{ \begin{array}{l} \text{Spontaneous} \\ \text{Equilibrium} \end{array} \right.$$

**We only need the sign of  $\Delta G$**





# Gibbs Free Energy

**A puzzle:**

at constant T and p,

$$\Delta G = \Delta E + p\Delta V - T\Delta S$$

Assume everything is reversible.

$$\Delta E = w + q$$

$$\Delta S = q/T$$

so  $\Delta G = w + p\Delta V$

but  $w = -p\Delta V$

Hence,  $\Delta G = 0$  ???

According to this, we can't ever have  $\Delta G < 0$  if everything is reversible at constant T and p. But what about all those chemical reactions? Surely they can be run reversibly! But  $\Delta G \neq 0$

Where is the mistake?



# What's the error?

## A puzzle:

at constant  $T$  and  $p$ ,

$$\Delta G = \Delta E + p\Delta V - T\Delta S$$

Assume everything is reversible.

$$\Delta E = w + q$$

$$\Delta S = q/T$$

so  $\Delta G = w + p\Delta V$

but  $w = -p\Delta V$

Hence,  $\Delta G = 0$  ???

Not all work is PV work! For example, electrochemical, mechanical, etc.

“Free” means free to do non-PV work!



# Temperature Dependence

First remember that:

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_P dT}{T}$$

$$\left( \frac{dq}{dT} \right)_P = C_P$$

If we hold P constant for a reversible process then:

$$\Delta G = V\Delta P - S\Delta T = - \int_{T_1}^{T_2} S(T) dT = - \int_{T_1}^{T_2} \left( S(T_1) + \frac{C_P}{T} \right) dT$$

This can be made even more exact if  $C_P(T)$  has been measured.



# Temperature Dependence

If we assume that  $\Delta S$  and  $\Delta H$  are constant over a small temperature range we can calculate  $\Delta G$  at different temperatures easily:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G(T) - \Delta G(298K) \approx -(T - 298K)\Delta S(298K)$$

*or*

$$\frac{\Delta G(T)}{T} - \frac{\Delta G(298K)}{298K} \approx \left( \frac{1}{T} - \frac{1}{298K} \right) \Delta H(298K)$$

Obviously, if  $\Delta S$  and  $\Delta H$  depend greatly on  $T$  then we must proceed as before!

# Temperature Dependence: Example

For glycl-glycine hydrolysis then:

$$\begin{aligned}\Delta S^\circ_{298} &= 2(103.51) - 190 - 69.5 \text{ J/(K mol)} \\ &= -52.9 \text{ J / (K mol)}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{298} &= 2(-537.2) - (-745.25) - (-285.83) \text{ kJ/(mol)} \\ &= -43.32 \text{ kJ / (mol)}\end{aligned}$$

Plugging and chugging!

$$\Delta G(37^\circ \text{C}) \approx (310 - 298)\Delta S(298\text{K}) + \Delta G(298\text{K}) = -26.99 \text{ kJ / mol}$$

$$\frac{\Delta G(37^\circ \text{C})}{310\text{K}} \approx \left( \frac{1}{310} - \frac{1}{298\text{K}} \right) \Delta H(298\text{K}) + \frac{\Delta G(298\text{K})}{298\text{K}} = -26.99 \text{ kJ / mol}$$

# Pressure Dependence: Example

For the pressure dependence we hold  $T$  constant:

$$dG \leq VdP - SdT = -VdP$$

Thus,

$$\Delta G = \int_1^2 VdP$$

And for an ideal gas:

$$\Delta G = \int_1^2 VdP = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln\left(\frac{P_2}{P_1}\right)$$

Does the free energy behave as expected?

Note that unlike in the puzzle,  $P$  is not constant!



Can we force graphite to diamond by increasing the pressure? We will use:

$$\Delta G = \int_1^2 V dP$$

and the fact that molar volumes of graphite and diamond are known:

$$\bar{V} = \text{weight} / \text{density}$$

$$\bar{V}_{\text{graphite}} = 5.33 \text{ cm}^3 / \text{mol}$$

$$\bar{V}_{\text{diamond}} = 3.42 \text{ cm}^3 / \text{mol}$$

$$\Delta G(P) = \Delta G(1 \text{ atm}) + \Delta V * (P - 1)$$

$$\Delta G(P) = 2.84 - 1.935 * 10^{-4} * (P - 1)$$

Where we have used a conversion factor to convert from  $\text{cm}^3 \text{ atm}$  to kJ.



Now, we want the pressure that makes  $\Delta G=0$ : *Why?*

$$0 = 2.84 - 1.935 \cdot 10^{-4} (P-1) \text{ kJ/mol}$$

$$P = 15,000 \text{ atm}$$

Experimentally, the required pressure is more! *Why?*



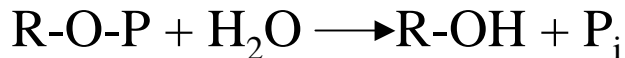


# Homework

Reading: Last half of Chapter 3, pp. 84-114, and Chapter 4, pp.123-134

TSW: 3.13, 3.22(d,f), 3.23,3.26

In a hypothetical cell, the steady-state concentrations of a phosphorylated intermediate, R-O-P, and its hydrolysis product, R-OH + P<sub>i</sub> are 0.02 M, 0.0004 M, and 0.05 M, respectively. The  $\Delta G^\circ$  of the hydrolysis reaction is -8.22 kcal/mol.



- a) Calculate the equilibrium constant for the hydrolysis reaction.
- b) Is the steady-state cited anywhere near equilibrium?
- c) Would you classify R-O-P as a high energy phosphate compound? Give  $\Delta G^\circ$  for the following reaction.

